Multistep Electroreductions of Fullerene C_{60} in the Ionic Liquid-Based Biphasic Systems

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Wide potential window, high ionic conductivity, which eliminates a need of using supporting electrolyte, and negligible vapor pressure, are the unique properties that make the room temperature ionic liquids (RTILs) attractive for electrochemical purposes [1]. Combining the RTILs with the processes of electrogenerated ion transfer across a liquid-liquid interface, may have an impact on the development of new electro-assisted extraction systems or ion selective amperometric sensors.

The aim of these studies was to determine the effect of RTIL on the ion transfer accompanying multistep reductions of fullerene C_{60} both deposited on the electrode surface as a solid film, and dissolved in a liquid phase. We focused on the ion-dependent electrochemical response that might be a starting point for a novel ion sensing system.

The RTILs investigated included water-immiscible phosphonium-phosphate ionic liquid [2], (C4mim)(NTf_2) and (C10mim)(NTf_2). Electrochemical experiments were performed both in the neat RTILs, and in the biphasic systems comprising of various aqueous electrolyte solutions in which the working electrode, coated with a small deposit of C_{60}/RTIL solution, was immersed.

In the biphasic arrangement three or four reduction steps of the C_{60} were observed on the voltammograms, depending on the RTIL used. The effect of the aqueous cations and anions on the subsequent C_{60} reduction-oxidation potentials was thoroughly examined for series of aqueous electrolytes. Interestingly, no significant dependence on the aqueous electrolyte was noticed, indicating similar values of the ion Gibbs energies of transfer from water to the RTIL. Only measurements in a wide range of concentrations of the aqueous electrolytes allowed us to deduce the type of transferring ion. Generally, the results suggest that in the presence of the RTIL the electrochemical reductions of both the solid and dissolved C_{60} proceed with the cation transfer from the aqueous phase to the ionic liquid environment. Surprisingly, when the RTIL was replaced by tetrahexylammonium perchlorate, the electrochemical response changed from the cation to the anion transfer mechanism [3, 4]. Additional experiments performed in the absence of the aqueous phase, enabled us to discuss the possible ion association between electrogenerated fulleride anions and constituents of the RTILs.

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